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Effect of experimental conditions on the parameters used for evaluating the performance of the catalyst Mo/Al_2O_3 in diesel soot combustion

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ABSTRACT

The literature reported different studies of soot combustion reaction under very distinct experimental conditions, which can include different values of catalyst:soot weight ratios, gas flow and heating rates. Therefore, avoiding screening of innumerable catalysts or empirical experiments, this work aims to present a general methodology based on a statistical experimental design of experiments with soot combustion, evaluating different reaction conditions and parameters that can be used for any other similar study. In this way, the effect of experimental conditions on the parameters used for evaluating the performance of Mo/Al_2O_3, a promising system previously studied, and Pt/Al_2O_3, a notorious catalytic system, were studied by a complete factorial experimental design. The results have shown that the experimental conditions strongly interfere with the parameters used for evaluating the catalytic performance and then it may generate incorrect conclusions.

The effects of interaction between different conditions on the activity and mainly on the selectivity of CO_2 permitted to explain the performance of catalysts on soot combustion and to distinguish different pathways of catalytic and non-catalytic reactions under specific reaction conditions.

The most appropriate conditions for studying soot combustion seem to be high cat:soot ratios, low heating rates and high gas flow rates, which, according to this work, must be equal to: 95:1, 2 K min^{-1} and 115 mL min^{-1}, respectively.

1. Introduction

Diesel-engine vehicles are very popular due to the relatively higher efficiency and durability of the engines as compared to gasoline ones. Diesel engines use oxidative mixtures with air/fuel ratios higher than 20, which result in relatively low-temperature combustion, so these engines produce low emissions of CO_2, NO_X, CO and hydrocarbons, however, the emission of particulate matter (PM) is high [1–2]. The effects of diesel particulate on health and the environment have stimulated the progressive establishment of severe emission standards [3,4].

In the last years, several catalytic systems have been studied for PM abatement [5–27]. Many authors have used differential thermal analysis (DTA) [5–7], and differential scanning calorimetry (DSC) [8–10], for evaluating the catalytic performances. In both cases, the parameter used for evaluating the catalytic performance is the temperature where the maximum of these peaks occurs that has been named combustion temperature (T_C). The catalytic effect, therefore, is verified by the decrease of the combustion temperature, comparing with the T_C of non-catalytic combustion reaction, which can be obtained using samples of PM alone or PM mixed with an inert material. In addition, it is possible to determine the CO_2 selectivity (S_{CO_2}) that is another useful parameter for the catalytic evaluation.

However, in both DTA and DSC analyses the sample is enclosed in a small crucible and, as a result, the gas feed flows around the sample and then heat- and mass-transfer limitations between the sample and the surroundings can occur [28]. Therefore, some authors have studied the PM combustion reaction using a test unit coupled to a gas analyzer [11–21], such as a mass spectrometer.

The soot combustion reaction involves several experimental variables, such as: the type of diesel particulate matter, catalyst:PM weight ratio; the way of mixing catalyst and PM; O_2 concentration in the gas phase (%vol); gas flow and heating rates. In fact, it can be verified in reported works that very distinct values of these experimental variables, i.e., distinct experimental conditions have been used for studying catalytic PM combustion reaction. So, the evaluation of the intrinsic performance of the reported catalytic systems is a difficult task.

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Some authors have used PM obtained from fuel combustion (real PM) [11,13,15–17,20,24–26], while others have used model PM, such as commercial carbon black [5–10,12,14,18,19,21–23]. Therefore, distinct values of the parameters used for evaluating the performance can be obtained from the same catalytic system if different real PM is used. The advantage of using a model PM is related to its constant properties that are fixed to commercial standard; moreover, the obtained T_C values can be directly related to the combustion of soot [29].

Several catalyst:PM weight ratios have also been reported, such as 2:1 [8,10,18,21]; 4:1 [5,21–23]; 10:1 [9,15,17,19,22]; 20:1 [6,11,12,13,16,20,24,27], and 100:1 [14]. It can be observed that the amount of the catalyst is higher than that of PM. This is in line with the real system, since it is expected that PM does not accumulate in the catalytic trap. So, different catalyst:PM ratios can affect the parameters used for evaluating the performance.

Considering the way of mixing catalyst and PM, it can be verified that several methods are reported, but they can be basically divided in two groups according to the degree of physical contact they promote between catalyst and PM. Some authors have mixed catalyst and PM using a ball mill [5,7,8], while others have obtained these mixtures by hand grinding in an agate mortar. These contacts have been referred as "tight" [6,9,11,16,17,20–23,27]. On the other hand, some authors have mixed catalyst and PM simply with a spatula [8,14,15,18,22–24], or shaking in a sample bottle [10,20], or even dipping catalyst in PM dispersion [22]. The contact generated has been named as "loose". Therefore, the distinct ways of preparing catalyst:PM mixtures can affect the parameters used for evaluating the catalytic performance since the contact between catalyst and PM can be a rate-limiting factor in PM combustion [8,29,30]. However, Neeft et al. [30], have reported that contact between PM and catalyst under practical conditions is poor. Then the study of catalytic PM combustion reaction using mixtures in "loose" contact can provide information with practical relevance [29].

Concerning other experimental conditions, the main variables are the O_2 concentration in the gas phase (%vol), gas flow rate and the heating rates. The values of O_2 concentration (%vol) in the gas phase reported in literature are about 6% [11,12,18–20,27], or about 20% [5–10,13,15–17,21,23,26], The gas flow rate values are in the range of 20–500 mL min^{-1} [5–24], while for the heating rates very different values are reported, such as 1 K min^{-1} [12], and 50 K min^{-1} [21]. In fact, at real conditions, the O_2 concentration (%vol) in diesel exhaustion is about 5–15%, the space velocity is very high and the temperature of the system at ideal conditions can be considered constant. As O_2 is a reactant in PM combustion, the O_2 concentration in the gas phase and the gas flow rate can really affect the parameters used for evaluating catalytic performance [31].

It is clear that catalytic PM combustion reaction have been studied at very distinct experimental conditions. Thus, although some catalytic systems presenting very promising performances have been reported, these performances may be related not only to the intrinsic catalytic properties but also to the experimental conditions used.

The effect of experimental conditions on the parameters used for evaluating the catalytic performance using the minimum number of experiments (*runs*), was proposed using a *full factorial design* of experiments [33,34].

In previous works [10,18], it was shown that the catalyst Mo/Al_2O_3 has promising performance for soot combustion, since it decreased the T_C of about 60 K and increased the S_{CO_2} from 30% to 75%, compared with non-catalytic combustion. In fact, the catalytic soot combustion is not a standard oxidation reaction and some notorious catalysts as Pt/Al_2O_3 are almost inactive [36,37]. There are different variables influencing mass and heat transport, kinetics, contact catalyst:soot and surface phenomena that may occur during soot combustion. If these parameters are not known and in order to minimize the experiments in soot oxidation of a real system, it is recommended to make a statistical design. In this design, generally, one has to be clear what the objectives are and then apply the correct model for a solution, and recommend the most appropriate conditions. Therefore, the main objective of this work is to determine the effect of each experimental condition and to verify the influence of the interchange parameters on the catalytic performance, allowing to selecting the most appropriate variables for evaluating the activity and selectivity of catalytic soot combustion, using a statistical experimental design. Temperature Programmed Oxidation (TPO) experiments were performed with the Mo/Al_2O_3 catalyst and the Pt/Al_2O_3 catalyst as a reference.

2. Experimental

Alumina C-type (Degussa AG) with specific area of 100 m^2 g^{-1} and MoO_3 (Aldrich) were used to prepare Mo/Al_2O_3 catalyst with 14% MoO_3 (wt.) by thermal spreading method, as described elsewhere [32]. The Pt/Al_2O_3 catalyst was prepared by wetness-impregnation using an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ and a commercial γ-alumina (170 m^2 g^{-1}). In addition, it was used as a model PM (Printex-V, Degussa AG), so the catalytic performance could be directly related to soot combustion.

Soot combustion reaction was studied by TPO experiments performed in a test unit using a fixed-bed quartz reactor coupled to a mass spectrometer Balzers/Prisma–QMS200 quadrupole. For the quantification of reactants and products, the area under the curves was related to the areas from curves of known volume pulses of the involved compounds. Quantification of CO ($m/e = 28$) was performed discounting the CO amount from CO_2 ($m/e = 44$) fragmentation. The CO and CO_2 curves of each TPO experiment were algebraically added and the area under the resulted curve was related to 100% of soot conversion in order to obtain a curve of percentage of soot conversion versus temperature. The parameters used for evaluating the catalytic performance, statistically named *responses*, were the CO_2 selectivity (S_{CO_2}) and the temperature where the maximum CO_2 formation occurs (T_C). In addition, the temperatures when soot conversion reached 10%, 25% and 50%, referred as T_{10}, T_{25} and T_{50}, respectively, were also studied as parameters for catalytic evaluation.

Aiming to study the effect of experimental conditions on the parameters used for evaluating the catalytic performance, a *full factorial design* of experiments was carried out [33,34]. All the catalyst:soot mixtures were prepared by gently mixing these compounds with a spatula in order to obtain a loose contact, which is similar to that verified in the real system. In addition, because of experimental limitations, the quantity of O_2 in the feed gas mixture was fixed to 5% O_2/He (V/V_0). Then, three experimental variables, or *factors*, were studied: catalyst:soot weight ratio (C:S), heating rate (H) and gas flow rate (F). For each variable, it was chosen two values based on the highest and the lowest reported ones, named minimum and maximum *levels*. For catalyst:soot weight ratio it was chosen 2:1 and 95:1; for heating rate, 2 and 20 K min^{-1}; and for gas flow rate the levels were 5 and 115 mL min^{-1}. Moreover, the soot combustion reaction was studied at an experimental condition where the medium values of all variables were used (C:S = 49:1, H = 11 K min^{-1} and F = 59 mL min^{-1}), also named *central point*. This experiment was replicated twice in order to estimate the experimental error. All the possible arrangement of the two levels of the three studied factors (2^3) plus the three experiments at central point condition resulted in eleven runs

performed with each catalyst in a random order, as statistically recommended [33].

All the catalyst:soot mixtures were pretreated at 473 K for 1 h under helium flow at 60 mL min^{-1}. Then, the systems were heated from room temperature to 923 K, under a gas flow of O_2/He, staying at 923 K until CO and CO_2 were no longer detected, i.e., until complete oxidation of the soot, which was confirmed with the carbon mass balance. The volume of the catalyst:soot beds were kept constant in order to have comparable values of residence times.

The effects of each experimental variable on the parameters used for evaluating the catalytic performance, named *main effects*, as well as the possible effects resulted from the *interaction* of two or three variables were determined using the software STATISTICA 6.0 [35]. For this calculation, the levels of the factors were coded as -1 (minimum value), 0 (medium value) and +1 (maximum value). It was also calculated the *P*-values, the probability of the effects being not ''real'', i.e., being only due to experimental variations. So, establishing 95% of minimum confidence, the main and interaction effects were considered real or significant when the *P*-values were lower or equal to 0.05 (i.e. 5%). For verifying if the statistical model was well adjusted, it was calculated *R*-values. *R*-values close to unit indicate that the statistical model was successfully fitted to the experimental data, given as *P*-values.

3. Results and discussion

Figs. 1 and 2 show the CO_2 formation profiles obtained from the soot combustion on Mo and Pt catalysts, respectively, carried out using different values of cat:soot ratio, heating rate and gas flow rate (C:S, H, F). The values used for each experimental variable are represented by the symbols +1 (maximum value), -1 (minimum value) and 0 (medium value). In addition, Table 1 correlates each set of experimental conditions employed with the parameters used for evaluating the catalytic performance obtained from the TPO profiles, i.e., the CO_2 selectivity (S_{CO_2}), the combustion temperature (T_C) and the temperatures corresponding to soot conversion of 10% (T_{10}), 25% (T_{25}) and 50% (T_{50}).

Table 1 presents the replicated runs performed at central point (CP) for the Mo catalyst. It can be verified that the medium value of S_{CO_2} is equal to (85 ± 4)% and of T_C is (859 ± 5) K. In addition, the medium values of T_{10}, T_{25} and T_{50} are (802 ± 7) K, (827 ± 10) K and (845 ± 6) K, respectively. The standard deviations obtained for these parameters indicate good reproducibility of the soot combustion experiments, even using loose contact cat:soot mixtures. Moreover, this table shows that the highest values of CO_2 selectivity were about 98%, and were obtained from all experiments performed with the minimum value of gas flow rate (runs 1–4), whereas the lowest values of T_C and also of T_{10}, T_{25} and T_{50} were obtained when the maximum

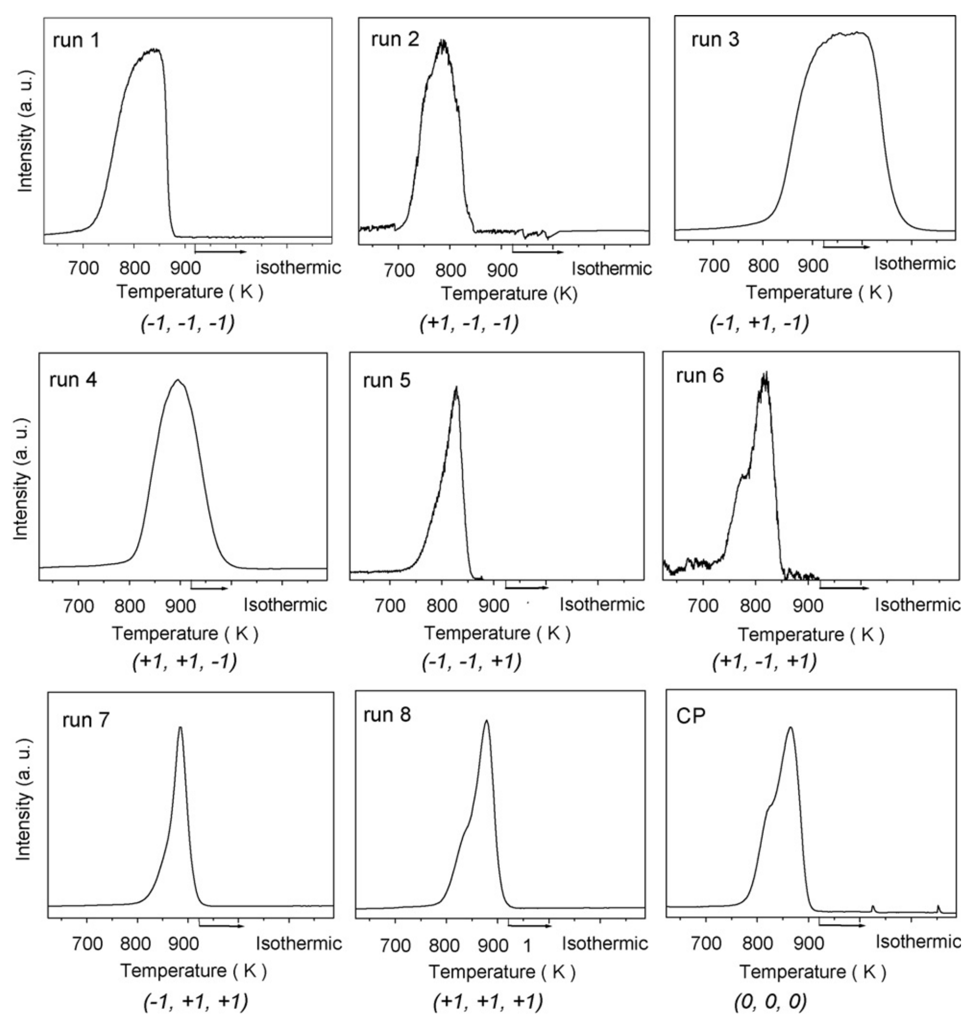

Fig. 1. –CO_2 formation profiles obtained from the catalytic soot combustion on Mo/Al_2O_3 catalyst carried out using different values of cat:soot ratio, heating rate and gas flow rate (C:S, H, F). The values used for each experimental variable are represented by the symbols +1 (maximum value), -1 (minimum value) and 0 (medium value).

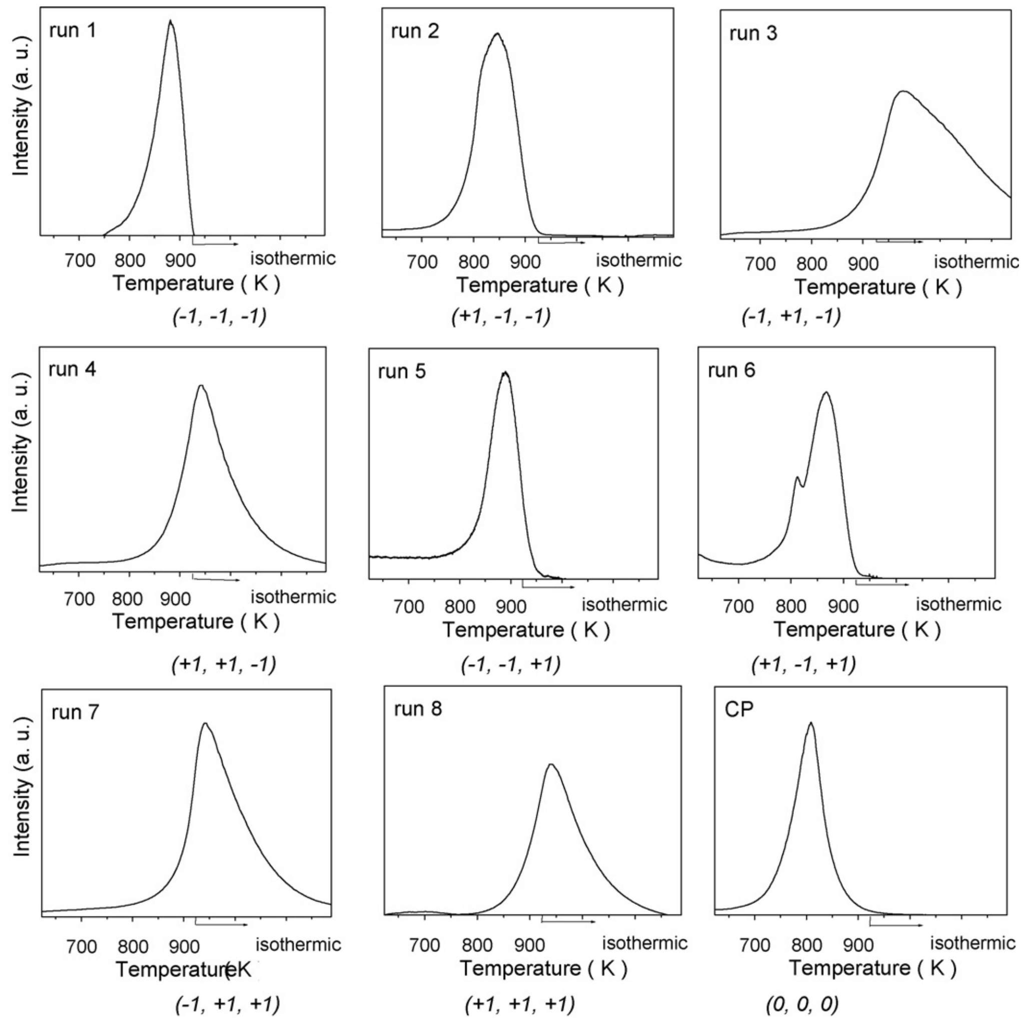

Fig. 2. –CO_2 formation profiles obtained from the catalytic soot combustion on Pt/Al_2O_3 catalyst carried out using different values of cat:soot ratio, heating rate and gas flow rate (C:S, H, F). The values used for each experimental variable are represented by the symbols +1 (maximum value), −1 (minimum value) and 0 (medium value).

cat:soot ratio, the minimum heating rate and the minimum gas flow rate values were employed.

In the case of Pt catalyst, the replicated runs performed at central point (CP) resulted in the medium value of S_{CO_2} equal to (87 ± 3)% and of T_C equal to (922 ± 5) K. In addition, the medium values of T_{10}, T_{25} and T_{50} are (864 ± 5) K, (892 ± 8) K and (917 ± 10) K, respectively. Once more, the standard deviations obtained for these parameters indicate good reproducibility of the soot combustion experiments, indicating a systematic preparation of the samples and adequate control of these conditions. Moreover, it is

Table 1

–CO_2 selectivity (S_{CO_2}), combustion temperature (T_C) and the temperatures corresponding to soot conversion of 10%, 25% and 50% (T_{10}, T_{25} and T_{50}, respectively) obtained from catalytic soot combustion carried out using different values of: cat:soot ratio (C:S), heating rate (H) and gas flow rate (F)

Runs	Coded factors			Responses									
	C:S[a] 2:1–95:1	H[a] 2–20 K min^{-1}	F[a] 5–115 mL min^{-1}	Mo					Pt				
				S_{CO_2}/%	T_C/K	T_{10}/K	T_{25}/K	T_{50}/K	S_{CO_2}/%	T_C/K	T_{10}/K	T_{25}/K	T_{50}/K
1	−1	−1	−1	98	856	768	792	815	92	882	815	847	973[b]
2	+1	−1	−1	97	787	738	757	778	92	847	796	818	843
3	−1	+1	−1	97	923	833	895	958[b]	88	978[b]	915	964[b]	1025[b]
4	+1	+1	−1	99	797	843	863	893	91	893	886	922	955[b]
5	−1	−1	+1	56	825	783	798	816	92	889	834	862	884
6	+1	−1	+1	75	821	768	787	805	98	867	806	832	858
7	−1	+1	+1	79	883	843	863	878	88	942[b]	904	935	968[b]
8	+1	+1	+1	93	879	833	848	868	90	940[b]	848	913	951
CP	0	0	0	82	853	794	836	839	85	927	870	900	927
CP	0	0	0	90	860	809	828	846	86	922	862	891	916
CP	0	0	0	83	863	803	816	851	91	918	860	884	908

These values of the factors are coded as: −1 (minimum), +1 (maximum) and 0 (medium).

[a] These values are the minimum and maximum values chosen for the experimental variables.

[b] These values were not real since the system was not heated over 923 K but these values were calculated as if the heating rate was constant until the end of the reaction.

Table 2
Statistical estimation results of the main and the interaction effects of each studied factors on the CO_2 selectivity (S_{CO_2}) the combustion temperature (T_C) and on the temperatures corresponding to 10%, 25% and 50% soot conversion on Mo/Al_2O_3 (T_{10}, T_{25}, and T_{50}, respectively)

Factors	S_{CO_2}		T_C		T_{10}		T_{25}		T_{50}	
	Main effect	*P*-value	Main effect	*P*-value	Main effect	*P*-value	Main effect	*P*-value	Main effect	*P*-value
C:S	**4.3**	**0.05**	**−25.4**	**0.008**	−5.6	0.08	**−11.6**	**0.03**	**−15.4**	**0.009**
H	**5.3**	**0.03**	**24.1**	**0.009**	**36.9**	**0.001**	**41.9**	**0.001**	**47.9**	**0.000**
F	**−11.0**	**0.004**	5.6	0.3	5.6	0.08	−1.4	0.7	−9.6	0.03
	Interaction effect	*P*-value	Interaction effect	*P*-value	Interaction effect	*P*-value	Interaction effect	*P*-value	Interaction effect	*P*-value
C:S × H	−0.3	0.7	−7.1	0.2	5.6	0.08	−0.1	1.0	−3.4	0.3
C:S × F	4.0	0.06	**23.4**	**0.01**	−5.6	0.08	**−10.4**	**0.04**	**−16.6**	**0.007**
H × F	**5.0**	**0.04**	4.9	0.3	−0.6	0.8	5.1	0.2	**10.1**	**0.03**
C:S × H × F	−1.0	0.5	7.1	0.2	−4.4	0.1	−0.88	0.8	3.6	0.3
Standard error	1.4		4.0		2.2		2.9		2.5	
R-value	0.987		0.988		0.995		0.994		0.997	

Numbers in bold are significant ($P < 5\%$).

interesting to notice that the CO_2 selectivity values are about 90%, basically independent on the experimental conditions. As in the case of the Mo catalyst, the lowest values of temperature were obtained when the maximum cat:soot ratio, the minimum heating rate and the minimum gas flow rate values were employed. Comparing the performance of the catalysts, it can be observed that, although promoting the CO_2 formation at high gas flow rate, the Pt catalyst did not promote the soot combustion at lower temperatures.

The influence that each experimental variable (factor) presents on the parameters used for evaluating the catalytic performance (main effect) and the influence that two or three experimental variables may simultaneously present on these parameters (interaction effects), i.e., S_{CO_2}, T_C, T_{10}, T_{25} and T_{50}, are presented in Tables 2 and 3 for Mo and Pt catalysts, respectively. In addition, these tables also exhibit *P*-values, the standard errors and the *R*-values.

Negative values of the main effects indicate that the factor and the response vary inversely, it means, when the value of the factor increases the value of the response decreases, or the opposite, when the value of the factor decreases the value of the response increases. On the other hand, positive values indicate that when the value of the factor increases the value of the response also increases or when the value of the factor decreases the value of the response also decreases.

In Table 2, it can be observed that *R*-values are about 0.99 in all cases, so the statistical model fits well to the experimental data. Considering the main effects of the studied factors on the S_{CO_2}, one noticed that the effect of the cat:soot weight ratio (C:S) is equal to 4.3 ± 1.4, which is close to the value of the main effect of the heating rate (H) (5.3 ± 1.4). In addition, the *P*-values calculated for these experimental variables are lower or equal to 0.05. So, it may be considered that the effects of the cat:soot weight ratio and of the heating rate on the S_{CO_2} are significant, and that an increase of the values of these variables promotes an increase of the CO_2 selectivity of the soot combustion reaction. On the other hand, the main effect of the gas flow rate is the greatest absolute value calculated (-11.0 ± 1.4) and its *P*-value is much lower than 0.05; so, the gas flow rate really influence the CO_2 selectivity and the higher the gas flow rate the lower the CO_2 selectivity. Therefore, these results permit to infer that the three experimental variables influence the CO_2 selectivity of soot combustion with the Mo/Al_2O_3 catalyst. It also suggests that the influence of the cat:soot weight ratio is related to the number of available active sites for soot combustion, whereas the influence of the heating rate is related to the rate of energy supply to the system. The influence of the gas flow rate may be related to the residence time of O_2. In fact, a strong influence was verified for the minimum value (5 mL min^{-1}, Table 1 – runs 1–4), resulting in a high residence time of O_2, which probably turns less important the influence of the other variables.

Concerning the interaction effects between two factors, positive values signalize that a high average value of response is obtained when both factors are studied at the maximum or the minimum value; moreover, positive values also mean that a low average value of the response is obtained when one factor is studied for the maximum and the other for the minimum value. Similarly,

Table 3
Statistical estimation results of the main and the interaction effects of each studied factors on the CO_2 selectivity (S_{CO_2}) the combustion temperature (T_C) and on the temperatures corresponding to 10%, 25% and 50% soot conversion on Pt/Al_2O_3 (T_{10}, T_{25}, and T_{50}, respectively)

Factors	S_{CO_2}		T_C		T_{10}		T_{25}		T_{50}	
	Main effect	*P*-value	Main effect	*P*-value	Main effect	*P*-value	Main effect	*P*-value	Main effect	*P*-value
C:S	1.4	0.4	**−18.0**	**0.05**	**−16.5**	**0.03**	**−15.4**	**0.01**	**−30.4**	**0.01**
H	−2.1	0.3	**33.5**	**0.009**	**37.8**	**0.03**	**46.9**	**0.0005**	**42.6**	**0.004**
F	0.62	0.7	4.8	0.4	−2.5	0.6	−1.1	0.7	−16.9	0.05
	Interaction effect	*P*-value	Interaction effect	*P*-value	Interaction effect	*P*-value	Interaction effect	*P*-value	Interaction effect	*P*-value
C:S × H	−0.12	0.9	−3.8	0.5	−4.8	0.4	−0.62	0.8	8.6	0.2
C:S × F	0.62	0.7	12.0	0.1	−4.5	0.4	2.4	0.5	**19.6**	**0.03**
H × F	−0.88	0.6	−2.0	0.7	−9.8	0.1	−8.4	0.6	1.6	0.8
C:S × H × F	−0.88	0.6	8.8	0.2	−2.3	0.6	2.6	0.4	−6.4	0.3
Standard error	1.5		5.5		4.3		2.8		5.3	
R-value	0.744		0.975		0.985		0.995		0.988	

Numbers in bold are significant ($P < 5\%$).

negative values of interaction effects result in a low average value of response, when both factors are studied at the maximum or at the minimum values, and also, negative values can signalize that a high average value of the response is obtained when one of the factors is studied at the minimum and the other at the maximum value.

Observing the interaction effects of two factors on the CO_2 selectivity, it is verified that there are no effects resulting from the interaction of the cat:soot weight ratio with the heating rate (C:S $\times$ H) nor from the interaction of the cat:soot weight ratio with the gas flow rate (C:S $\times$ F), although the effect related to the interaction between the heating rate and the gas flow rate (H $\times$ F) is significant (P-value ≤ 0.05) and positive (5.0 ± 1.4). So, experiments carried out with the maximum values of these variables result in relatively high CO_2 selectivity (Table 1 – runs 7 and 8). However, as observed the effect of the gas flow rate is strong and negative (Table 2); thus, experiments carried out using the maximum value of gas flow rate result in low CO_2 selectivity. Therefore, these results may suggest that, although a high gas flow rate may disfavor the CO_2 selectivity, since it causes a low contact time of O_2 with soot, when a high gas flow rate is associated to a higher heating rate, the energy supply to the system would accelerate the reaction and promote a higher CO_2 selectivity. The results presented in Table 2 indicate that there are not significant effects resulting from the interaction of the three factors (C:S $\times$ H $\times$ F) on the CO_2 selectivity and also on other parameters for the evaluation the catalytic performance.

Concerning the combustion temperature (T_C), one can observe effects of the cat:soot weight ratio and the heating rate, but the absolute values are very similar (-25.4 ± 4.0 and 24.1 ± 4.0, respectively). However, these factors influence the T_C in different ways. The main effect of the cat:soot ratio is negative, i.e., the higher the amount of catalyst in the cat:soot mixture the lower is the T_C value; the main effect of the heating rate is positive, i.e., the higher the heating rate the higher the T_C value. In fact, the heating rate influences strongly not only the T_C but also the CO_2 profiles that are shifted to higher temperatures as the heating rate increases (compare, for example, the profiles from runs 5 and 7 – Fig. 1). These changes in TPO profiles are similar to those reported for DTA and DSC curves [31].

Concerning the interaction effects of two factors on the T_C, one can observe that the interaction between the cat:soot ratio and the gas flow rate is significant (P-value = 0.01) presenting a positive value. However, this is a remarkable result, because the main effect of the cat:soot ratio is significant and negative, while the main effect of the gas flow rate is not significant. In fact, this apparent ambiguity can be understood observing the CO_2 profiles (Fig. 1). As shown, some profiles obtained from experiments, using the minimum value of the gas flow rate (see the profiles from runs 1 and 3), do not present well-defined maximum of CO_2 formation, which may be related to a reaction limitation, since the available O_2 in the same temperature range was totally consumed. Therefore, in these cases, one must be cautious, because it was difficult to identify the combustion temperature, which may influence the calculated effects of these factors on T_C. Moreover, as observed in Fig. 1, the reaction limitation is clearly seen for run 3, although performed at the same conditions of run 1, except for the heating rate. So, it seems that high heating rates would increase the rate of O_2 consumption, resulting in reaction limitation. On the other hand, the CO_2 profiles performed with the minimum gas flow rates (runs 2 and 4) do not clearly show reaction limitations. Thus, reaction limitation seems to be mainly related to the minimum value of gas flow rate associated with the minimum value of cat:soot weight ratio (compare CO_2 profiles from runs 1 and 2, and from runs 3 and 4).

The CO_2 profiles obtained from experiments performed at the maximum gas flow rate (runs from 5 to 8), show that they are very similar and present a well-defined temperature of maximum CO_2 formation (T_C). It can be observed that the experiments performed at the same conditions but with different cat:soot weight ratios (compare profiles of runs 5 with 6 and runs 7 with 8), affect significantly the CO_2 profiles. Thus, for the maximum value of cat:soot weight ratio the profiles exhibit a shoulder at low temperatures. Considering that both catalytic and non-catalytic reactions may occur simultaneously during soot combustion, it can be suggested that the shoulder at low temperature may be related to a catalytic reaction, since more active sites are available for the reaction, when higher amounts of catalyst in the cat:soot mixture are used. Moreover, considering that the Mo/Al_2O_3 catalyst presents distinct Mo active species, as reported previously [18], one can also suggest that this behavior can be attributed to different active species. Fig. 1 shows also that the CO_2 profile for the central point condition is similar to the condition of the maximum gas flow rate and maximum cat:soot weight ratio (runs 6 and 8).

Table 2 presents the main effects of the experimental variables on the T_{10}, the T_{25} and the T_{50}. It can be observed that the heating rate has a significant effect on all these parameters, as discussed above. Also, the effect of gas flow rate is only significant for T_{50}, presenting a negative value. As the reaction rate occurs around the maximum, at about 50% of conversion, this negative result indicate that high gas flow rates promote better heat-transfer, although the reaction limitation cannot be discarded. The main effect of the cat:soot weight ratio is significant for both T_{25} and T_{50}, but insignificant for T_{10}. In fact, it seems that at low temperature mainly the catalytic reaction occurs instead of non-catalytic, but the reaction rate is still low and therefore the T_{10}, which is close to the onset temperature, probably depends more on the nature of the catalytic sites than of the amount of catalyst in the system. On the other hand, for higher temperatures where both catalytic and non-catalytic reactions may occur the amount of catalyst has a more important effect.

The effects of interaction between weight ratios and heating rates on T_{10}, T_{25} and T_{50}, are insignificant. On the other hand, the interaction between the heating rate and the gas flow rate is only significant for T_{50}, presenting a positive value. That means, high gas flow rates tend to decrease the T_{50}, by improving the heat-transfer, while high heating rates displace the CO_2 profile to higher temperatures. Finally, the interaction effect between cat:soot weight ratio and gas flow rate is significant on T_{25} and T_{50}. The reaction rate at T_{25} is significant but higher at T_{50}. High cat:soot weight ratios contain more active sites, favoring the catalytic reaction, and disfavor hot points. These effects associated with a better heat-transfer effect due to high gas flow rates would result in lower values of T_{25} and T_{50}. In addition, high gas flow rates improve the mass transfer and consequently there is not the limiting rate in this process, increasing the activity and so reducing ignition temperature. It also promotes the contact with the active sites, facilitating the reaction.

In the case of the Pt catalyst, one can observe (Table 3) that the R-values are about 0.99, except for the CO_2 selectivity, where R is 0.74. Moreover, the values of the interaction effects for the experimental conditions on the S_{CO_2}, are not significant. This model does not fit well the data for CO_2. Results agree with the almost invariant values of S_{CO_2} for the Pt catalyst (Table 1).

The effect of heating rate on the T_C, T_{10}, T_{25} and T_{50} is positive, and the catalyst:soot weight ratio is negative. In addition, only the T_{50} is significantly affected by the gas flow rate and the interaction between the cat:soot weight ratio and gas flow rate. This may be related to a better heat transfer for maximum gas flow rate and cat:soot ratio.

The CO_2 profiles in Fig. 2 show that profiles are very similar. Indeed, the asymmetric form of these profiles is an indication of

multiple processes taking place during the oxidation of soot. The CO_2 base profile of run 3 is large at a high temperature range, suggesting that the reaction rate is low for this condition. The profile of run 6 reveals clearly the presence of a shoulder at low temperature, which can be attributed to a different pathway of soot combustion, preferentially the catalytic reaction at lower temperatures.

There are some differences but also many coincidences, comparing the effects of the experimental conditions on the soot combustion of both catalysts. The gas flow rate seems to be important for the Mo catalyst, influencing strongly the CO_2 selectivity and limiting the reaction rate at low gas flow rates, however, it does not affect significantly the performance of the Pt catalyst. These results seem to be in line with the intrinsic activity of Pt for oxidation of CO to CO_2 and may indicate that the effect of the experimental conditions on CO_2 selectivity depends on the nature of the catalytic material.

The effects of the experimental conditions on the temperature of soot combustion are similar. Both catalyst to soot ratio and the heating rate exert strong influence on the temperature, independent on the catalytic system. One can conclude that the temperatures T_C, T_{10}, T_{25} and T_{50} are important parameters for evaluation of the catalytic performance, because they are related to different steps of the soot combustion, however, the experimental errors associated to the determination and conditions at which they were obtained should be considered.

The choice of the most appropriate experimental conditions for catalytic soot combustion using Temperature Programmed Oxidation must take into account the real conditions of soot combustion in a catalytic converter. For real conditions one can expect that soot does not accumulate in the trap to prevent pressure drop [2], and therefore, it is more appropriate to use high cat:soot weight ratios; high gas flow rates, keeping high space velocity of exhausting compounds. In addition, the exhaust temperature can be considered around 573 K and programming low heating rates, which represent these conditions. In this work, these conditions are better represented, using cat:soot ratio 95:1; heating rate of 2 K min^{-1} and the gas flow rate of 115 mL min^{-1}. Noteworthy is that these conditions were performed with both catalysts, yielding CO_2 profiles with a shoulder (run 6, Figs. 1 and 2). In the particular case of Mo catalysts, runs 6, 8 and CP (Fig. 1) evidence shoulder in the CO_2 profile, where the maximum or the medium values of cat:soot weight ratios and gas flow rates were used, but the temperature range of the reaction is also influenced by the heating rate. Thus, CP profile can be used to study the soot combustion without losing too much information about the catalytic reaction and saving material since it was used the medium values of the cat:soot ratio and the gas flow rate (49:1 and 59 mL min^{-1}, respectively), reducing the amount of catalysts and gas mixture. However, the high effect of heating rate on the results indicate that should be more interesting to use the minimum value (2 K min^{-1}) Therefore, these conditions are the most suitable and should be carefully controlled in order to give important data about the surface phenomena and kinetics with comparable experimental parameters for evaluating soot combustion, avoiding heat and transfer limitations. On the other hand, this methodology is reliable for TPO experiments. Although the conditions suggested in this paper might change for other catalytic system, the evaluation of the performance may consider the effects of experimental conditions quantified here.

4. Conclusion

This statistical experimental design methodology allows to selecting the most appropriated conditions for soot combustion, which is easily applied for any other system for the evaluation of the performance of a catalyst under real conditions. If used as standard experimental condition allows us to compare different experiments with catalysts and distinct catalytic systems.

The effects of interaction between different parameters on the activity, the onset and combustion temperatures and mainly on the selectivity of CO_2 permitted to explain the performance of soot combustion under different conditions. These results have also shown that it may possible to distinguish different pathways of catalytic and non-catalytic reactions under specific reaction conditions.

Therefore, from the statistical experimental design methodology it was possible to choice the most appropriate conditions for the real catalytic soot combustion that are: high cat:soot ratios, low heating rates and high gas flow rates, which, according to this work, must be equal to: 95:1, 2 K min^{-1} and 115 mL min^{-1}, respectively.

These conditions are the most suitable for the catalytic performance for soot combustion, avoiding heat and transfer limitations and reliable in TPO experiments. On the other hand, this methodology is recommended for other reaction systems to have a first idea about catalytic performance on soot combustion at real conditions.

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References

[1] P. Degobert, Automobiles and Pollution, SAE, Warrendale, PA, 1995.
[2] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Fuel Process. Technol. 47 (1996) 1.
[3] P. Greening, Top. Catal. 16 (2001) 5.
[4] B.I. Bertelsen, Top. Catal. 16 (2001) 15.
[5] R. Flouty, E. Abi-Aad, S. Siffert, A. Aboukaïs, Appl. Catal. B 46 (2003) 145.
[6] K. Sato, M. Yamaguchi, S. Fujita, K. Suzuki, T. Mori, Catal. Commun. 7 (2006) 132.
[7] H. Laversin, D. Courcot, E.A. Zhilinskaya, R. Cousin, A. Aboukaïs, J. Catal. 241 (2006) 456.
[8] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Appl. Catal. B 8 (1996) 57.
[9] D. Fino, N. Russo, E. Cauda, G. Saracco, V. Specchia, Catal. Today 114 (2006) 31.
[10] S. Braun, L.G. Appel, M. Schmal, Catal. Commun. 6 (2005) 7.
[11] E.E. Miró, F. Ravelli, M.A. Ulla, L.M. Cornaglia, C.A. Querini, Catal. Today 53 (1999) 631.
[12] Y. Teraoka, K. Kanada, S. Kagawa, Appl. Catal. B 34 (2001) 73.
[13] G. Neri, G. Rizzo, S. Galvagno, A. Donato, M.G. Musolino, R. Pietropaolo, Appl. Catal. B 42 (2003) 381.
[14] S. Liu, A. Obuchi, J. Uchisawa, T. Nanba, S. Kushiyama, Appl. Catal. B 37 (2002) 309.
[15] B. Dernaika, D. Uner, Appl. Catal. B 40 (2003) 219.
[16] V.G. Milt, C.A. Querini, E.E. Miro, Thermochim. Acta 404 (2003) 177.
[17] P. Ciambelli, V. Palma, P. Russo, S. Vaccaro, J. Mol. Catal. A 204 (2003) 673.
[18] I.C.L. Leocadio, S. Braun, M. Schmal, J. Catal. 223 (2004) 114.
[19] J. Liu, Z. Zhao, C. Xu, A. Duan, L. Zhu, X. Wang, Appl. Catal. B 61 (2005) 39.
[20] M.A. Peralta, V.G. Milt, L.M. Cornaglia, C.A. Querini, J. Catal. 242 (2006) 118.
[21] C. Badini, G. Saracco, N. Russo, V. Specchia, Catal. Lett. 69 (2000) 207.
[22] H. An, P.J. McGinn, Appl. Catal. 62 (2005) 46.
[23] A. Bueno-López, K. Krishna, M. Makkee, J.A. Moulijn, J. Catal. 230 (2005) 237.
[24] K. Tikhomirov, O. Kröcher, M. Elsener, A. Wokaun, Appl. Catal. B 64 (2006) 72.
[25] Y. Zhang, X. Zou, Catal. Commun. 7 (2006) 523.
[26] G. Corro, J.L.G. Fierro, F.B. Romero, Catal. Commun. 7 (2006) 869.
[27] E. Aneggi, C. Leitenburg, G. Dolcetti, A. Trovarelli, Catal. Today 114 (2006) 40.
[28] J.P.A. Neeft, F. Hoornaert, M. Makkee, J.A. Moulijn, Thermochim. Acta 287 (1996) 261.
[29] B.A.A.L. van Setten, J.M. Schouten, M. Makkee, J.A. Moulijn, Appl. Catal. B 28 (2000) 253.
[30] J.P.A. Neeft, O.P. van Pruissen, M. Makkee, J.A. Moulijn, Appl. Catal. B 12 (1997) 21.
[31] F.W. Wilburn, J.H. Sharp, D.M. Tinsley, R.M. McIntosh, J. Therm. Anal. 37 (1991) 2003.
[32] S. Braun, L.G. Appel, V.L. Camorim, M. Schmal, J. Phys. Chem. B 104 (2000) 6584.
[33] B. Barros, I.S. Scarminio, R.E. Bruns, Como Fazer Experimentos: Pesquisa e Desenvolvimento na Ciência e na Indústria, UNICAMP Ed., Campinas, 2003.
[34] L.S. Sutherland, C. Guedes Soares, Compos. Sci. Technol. 63 (2003) 1.
[35] StatSoft Inc., 2325 East 13th Street, Tulsa, OK, USA.
[36] U. Hoffmann, J. Ma, Chem. Eng. Technol. 13 (1990) 251.
[37] A.F. Ahlstrom, C. U. I. Odenbrand, Appl. Catal. 60 (1990a) 143.